5(1, 2)
AUTHORS: Korshunov, I. A., Vertyulina, L. N., SOV/20-122-6-20/49
Razuvayev, G. A., Corresponding Member, AS USSR,
Sorokin, Yu. A., Domrachev, G. A.

TITLE: Polarographic Reduction of Some Chromium Aromatic Compounds of Sandwich Structure (Polyarograficheskoye vosstanovleniye nekotorykh khromaromaticheskikh soyedineniy sendvichevogo stroyeniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 6, pp 1029-1031 (USSR)

ABSTRACT: While the polarographic behavior of the bis-cyclopentadienyl compounds was described sufficiently in detail (Ref 1), there is one paper only (Ref 2) on the reduction of the cation $((C_6H_6)_2Cr)^+$. As in the laboratory of the authors dibenzene-(I)-, ditoluene-(II), dimesitylene-(III)-and bis-diphenyl chromium-(IV) iodide were prepared, furthermore the dicumene-(V)-and di-(cyclohexyl benzene)-chromium iodides-(VI) not described in publications, it was interesting to study the polarographic reduction of this series of compounds. The synthesis (according to Ref 3) of the above-mentioned

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derivatives ((I)-(VI)) is described together with the yields computed and ascertained. From the concentrated solution of dicumene chromium the compound (V) was precipitated as a cherry-red viscous oil by adding saturated aqueous KJ-solution. The authors did not succeed in crystallizing it. (V) is well soluble in low alcohols, acetone, methylene chloride, dichloro ethane, pyridine, dimethyl formamide, whereas it is practically insoluble in ether, CCl_4, water and benzene.

(VI) is synthesized by a similar method. (VI) was isolated as a dark-red powder from the reaction mixture (with an addition of 50 ml purified n-nonane) by heating for 1.5 hours at 150°. Its solubility in the solvents mentioned in connection with (V) is the same as that of (V). The polarographic investigations of the iodides ((I)-(VI)) were carried out by means of the visual polarograph, which is manufactured by the institute mentioned in the Association. The reduction was carried out on the background of several 0.5 N aqueous electrolytes of lithium chloride, sodium hydroxide, potassium nitrate, sodium sulfate, hydrochloric acid and buffer

solutions with pH from 2.3 to 11.75 (Fig 2). The chromium aromatic compounds produce diffusion currents in almost all above-mentioned electrolytes. An exception are hydrochloric acid and the buffer solutions with a pH-value below 2, in which they are precipitated or (e. g. (II)) do not develop any reduction waves. All iodides are reduced within one wave (Fig 1). From the study of the results obtained it can be concluded that the introduction of the alkyl-(V) or cyclohexyl-(VI) substitutent into the aromatic nucleus does not exercise considerable influence upon the quantity of the semiwave--potential. In the transition from (II) to (III) the semiwave is shifted only slightly into the direction of the negative values as compared with (I). In the introduction of an aromatic substituent (IV), however, a marked shift of the potential into the range of positive values takes place. For the time being, it is still difficult to reconcile the polarographic results with the data obtained by other methods. The polarographic method, however, can play a certain role in the investigation of the nature of the class of

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compounds in question. There are 3 figures and 4 references, 1 of which is Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii Gor'kovskogo gosudarstvennogo universiteta im. N. I. Lobachevskogo (Scientific Research Institute of Chemistry of the Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: June 17, 1958

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RAZUVAYEV, G.A.; MINSKER, K.S.; FEDOSEYEVA, G.T.; SAVEL'YEV, L.A.

Effect of amines on the stereospecific polymerization of propylene.
Vysokom.soed. 1 no.11:1691-1695 N '59. (MIRA 13:5)
(Propene) (Amines)

SOV/79-29-5-10/75

5(4)
AUTHORS: Svetozarskiy, S. V., Zil'berman, Ye. N., Razuvayev, G. A.

TITLE: Low-Temperature Autocondensation of Cyclohexanone (Nizkotemperaturnaya avtokondensatsiya tsiklogeksanona)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1454 - 1457 (USSR)

ABSTRACT: In the present paper a $C_{18}H_{30}O_3$ compound (I) was obtained by means of autocondensation of cyclohexanone at room temperature in the presence of solid sodium hydroxide as catalyst. It represents a tricyclic product with a carbonyl- and two ternary hydroxyl-groups. On heating with solid sodium hydroxide (I) decomposes to give cyclohexanone and 3-cyclohexylidene—cyclohexanone. Owing to the reaction of (I) with concentrated sulfuric acid as well as on short heating 2 water molecules are splitted off and an unsaturated $C_{18}H_{26}O$-ketone (II) is formed.

On protracted heating of (I) and (II) the dodecahydro-1,2,3,4,5,6,7,8,9,10,11,12-triphenylene (III) is formed in good yield. Owing to the transformation of (I) into (III) the com-

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pound $C_{18}H_{30}O_3$ must be a dioxy-ketone with the structure of the 2-[2-(1-oxy-cyclohexyl)-1-oxy-cyclohexyl]-cyclohexanone (Fig 1). The easy transformation of (II) into (III) may be due to steric factors. In order to define the structure of the ketone (II) its ultraviolet spectrum in diethyl ester (Fig 2) was taken. It was found that (II) can only have the structure of 2-[2-(Δ'-cyclohexenyl)-cyclohexylidene]- cyclohexanone. No usual derivatives of carbonyl compounds could be obtained from the ketone (II) and the dioxy-ketone (I) which is due to steric hindrances. It has to be mentioned that (III) is usually obtained in a yield of 6% at the most (Ref 3). The transformations of (I) and (II) into (III) here described are a new and convenient method for the preparation of dodecahydrotriphenylene. The authors express their gratitude to Ts. N. Roginskaya for taking the ultraviolet spectra. There are 3 figures and 9 references, 1 of which is Soviet.

SUBMITTED: April 11, 1958

SOV/79-29-9-37/76

5(3)

AUTHORS: Kazuvayev, G. A., Spasskaya, I. F., Etlis, V. S.

TITLE: Chlorination of the α-Chloro Aldehydes

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2978-2980 (USSR)

ABSTRACT: The chlorination of aliphatic aldehydes has hitherto been little investigated (Refs 1-4) in contrast to the well-known chlorination of aromatic aldehydes into the corresponding acid chlorides. Only individual cases are described in which the carbonyl hydrogen of the aliphatic aldehydes is replaced by chlorine. As in the chlorination of the carbonyl compounds halogen is substituted for hydrogen on carbon in α-position to the carbonyl, the chlorination of several α-chlorine-substituted aldehydes was of practical interest. The acid chlorides of dichloroacetic and α,α-dichloropropionic acid were obtained in good yields and with small impurities of free acid from chlorination in ultraviolet light as well as in the presence of acetylcyclohexane sulphonyl peroxide at 50-60°. These acid chlorides were obtained from dichloro acetic and α,α-dichloropropionaldehyde. The chlorination of α,α-dichloropropionaldehyde is accompanied by a marked decarbonylization under the formation of 1,1,1-tri-

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chloro ethane and phosgene. The formation of the products found may take place according to the scheme $R'CCl_2CHO + R^{\cdot} \longrightarrow R'CCl_2\dot{C}O + RH$ (Ref 4), where R' = H, CH_3; $R^{\cdot}$ = a chlorine atom or a free radical formed by cleavage of the peroxide or by photolysis of the aldehyde. The α,α-acyl dichloride radicals react with chlorine and form acid chlorides of α,α-dichlorine-substituted acids: $R'CCl_2\dot{C}O + Cl_2 \longrightarrow R'CCl_2C(=O)Cl + Cl$. The cleavage of a considerable part of the radicals $CH_3CCl_2\dot{C}O$ takes place at 50-60° according to the scheme $CH_3CCl_2\dot{C}O \longrightarrow CH_3\dot{C}Cl_2 + CO$. The cleavage products react with chlorine and form 1,1,1-trichloro ethane and phosgene (last scheme). Thus, the chlorination of the anhydrous α,α-dichlorine-substituted aldehydes leads, under the above conditions, to the formation of the acid chlorides of α,α-dichlorine-substituted acids in good yields and may be preparatively applied to those cases in which other chlorinating agents are not desired. As far as the

Chlorination of the α-Chloro Aldehydes

chlorination of the α-monochlorine-substituted aldehydes is concerned, an experiment was only possible with the acetaldehyde available (with 5-6% water); in the chlorination dichloroacetic acid formed predominantly besides a small quantity of dichloroacetyl chloride. There are 1 table and 14 references, 2 of which are Soviet.

SUBMITTED: August 11, 1958

SOV/79-29-9-38/76

5(3)

AUTHORS: Razuvayev, G. A., Petukhov, G. G., Osanova, N. A.

TITLE: Investigation of the Reactions of Pentaaryl Phosphorus. Determination of the Equivalence of the Groups by Means of Deuterium

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2980-2983 (USSR)

ABSTRACT: The investigation of the reactions of pentaaryl phosphorus with deuterium in a phenyl group in benzene- or chloroform solution showed that the separation of both the polar and the equatorial phenyl groups takes place equally easily and with radical mechanism (Ref 1). The problem arose whether in ionic separation of pentaphenyl phosphorus the equivalence of the polar and equatorial phenyl groups was maintained. The reaction of pentaphenyl phosphorus with hydriodic acid (Ref 2) and acetic acid (Ref 1) is known to be an ionic reaction. The reactions of this phosphorus compound containing deuterium in a phenyl group with the above acids actually showed that the equivalence of the polar and equatorial groups is also observed in the course of an ionic reaction. The quantity of deuterium in dinitrobenzene obtained from the separated phenyl groups amounts to approximately 1/5 of the total quantity of deuterium in pentaphenyl phos-

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phorus as may be seen from the data of table 1 (experiments 1,2). J. Wittig substituted the p-tolyl group for a phenyl group and found in the reaction of tetraphenyl tolyl phosphorus with hydrobromic acid (Ref 2) that besides benzene and toluene a mixture of triphenyl-p-tolyl- and tetraphenyl phosphonium bromide results (3:1). Information on the ratio of benzene to toluene is, however, missing in his report as well as the method of determining the ratio of the salts in the reaction products. The authors assumed that such a ratio of the separated phenyl- to the tolyl groups with tagged atoms could be determined. For this purpose a tetraphenyl-p-tolyl phosphorus with a deuterium atom in the cycle of the tolyl group was synthesized and caused to react with hydrobromic acid, chloroform, and alcohol. The table (columns 5,9) gives data on the distribution of deuterium in products obtained from the separated radicals, and in the radicals which remained linked to the phosphorus, on the assumption of equivalent separation of the tolyl- and phenyl groups. A comparison of these data with those experimentally obtained (Table, experiment 3) shows that in ionic reactions (in

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this case in the reaction with HBr (Table, experiment 3)) there is no difference in the rate of separation between the tolyl- and phenyl groups of tetraphenyl-p-tolyl phosphorus. In chloroform, where the reaction takes place according to the radical mechanism, separation of the phenyl radicals is predominant (Table, experiments 4,5). There are 1 table and 3 references, 1 of which is Soviet.

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet (Gor'kiy State University)

SUBMITTED: July 21, 1958

5 (3)

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR, Petukhov, G. G., Zateyev, B. G.

SOV/20-127-2-31/70

TITLE: On the Interaction Between Phenyl Radicals and Benzene

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 348-351 (USSR)

ABSTRACT: The interaction between the radicals produced in the occurring dissociation of the initial compound (R:R) (under the influence of temperature, light, etc) and the medium solvent (X:S) is very important in the free radical reactions. This problem has been investigated as late as in most recent time in spite of its importance. 1) the initial substance can form an intermediate complex with the solvent [R : RX : S] which will homolytically decompose in free shape into RX and RS without separation of radicals. 2) The substance [R : R] can be solvated. In its decomposition into radicals the latter can enter into an interaction in a "cell" without transition into the volume of the solvent. Finally the radicals can pass over from this "cell" into the volume of the solvent and form with the latter an intermediate complex there [R · X : S]. In this case the radicals may cause chain processes. The radical transition can be caused by the transition of the peripheric atom of the solvent X to the

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radical R. The system in which R = S is a special case. By this the radical is regenerated and its kinetic duration of life is prolonged. The authors investigated in the present paper the topic mentioned in the title by the example of several compounds which decompose homopolarly under separation of the phenyl radical. The method of marked atoms was used in order to prove the reaction of the radical transition. C^{14} was for this purpose introduced into the initial compound as well as into benzene, i.e. 2 systems were investigated: a marked dissociating compound and inactive benzene, and an unmarked compound and active benzene. 3 types of the interaction mentioned in the title can be assumed here (see Scheme (I) - (III)). Among them the reaction (III) is anew experimentally confirmed (Ref 3). However, the occurrence of process (III) does not eliminate reaction (II). It is very probable that the first stage of the interaction will be the formation of the π-complex (IV) which can pass over into a σ-complex (III) if the radical transition does not proceed in it. By the example of diphenyl mercury (DPhM) (Refs 4, 5) it was proved that diphenyl was produced only by DPhM. Benzoyl peroxide (BP) is another source of phenyl radicals. Its reaction with benzene is rather complicated and several products or their

mixture are produced. Although the phenyl radicals from BP were predominant, a part of the BP phenyl radicals escaped nevertheless as benzene into the volume on the strength of the reaction (II). The reaction of the initiated mercury acetate decomposition was used in order to prove this process better (Ref 7). A small quantity of terphenyl and quaternary phenyl is produced besides diphenyl. Since a disagreement in the number of isotopes of the di- and quaternary phenyl was striking it could be assumed that quaternary phenyl was not produced by diphenyl by its subsequent phenylation. This was experimentally confirmed. The formation of quaternary phenyl requires, however, further investigations. Finally the influence of ultraviolet light and of lead tetrabenzoate is discussed. There are 1 table and 8 references, 5 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete (Scientific Research Institute of Chemistry at the Gor'kiy State University)

SUBMITTED: March 18, 1959

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SOV/20-127-3-28/71

5(2,3)

AUTHORS: Razuvayev, G. A., Corresponding Member, AS USSR, Bobinova, L. M., Etlis, V. S.

TITLE: Some Chemical Properties of Phenyltitantriisopropylate and Its Catalytic Power in the Polymerization of Olefines

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3, pp 581 - 583 (USSR)

ABSTRACT: It was proved that diphenyltitancyclopentadienyl alone (Refs 1,2) cannot initiate a polymerization of ethylene. If titantetrachloride is added to trialkylaluminum, catalysts develop in both cases which transform ethylene into a solid polymer. $(C_6H_5)_2Ti(C_5H_5)_2$ differs considerably from the usual metal-organic compounds with co-valent Me-C-linkages as far as its structure is concerned. Phenyltitantriisopropylate is a purely co-valent titan-organic compound (Refs 3,4) and is an initiator of the polymerization of styrene into a solid polymer. Some investigators explain this by the readiness to decompose with the development of a phenyl radical. Since the chemical reaction characteristic of true metal-

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organic compounds have been little investigated as far as phenyltitantriisopropylate is concerned, the authors carried out the present work. They investigated its catalytic power for unsaturated compounds, alone and with an addition of AlR_3 or $TiCl_4$, and also its chemical properties. The mentioned product, synthesized by the authors, actually initiated the polymerization of styrene, but during the reaction with propylene, only traces of a liquid polymer could be found. This catalyst also polymerized several tested monomers. It was proved that the system $Al(C_2H_5)_3$ - $C_6H_5Ti(i\text{-}OC_3H_7)_3$ initiated the polymerization of propylene at 9o-100° with the development of not more than 3o-35% of a liquid polymer. The addition of titantetrachloride to phenyltitantriisopropylate developed a catalyst which caused a more intensive polymerization of propylene at 9o-1oo°. The liquid polymer had a molecular weight of 144-545. Its output largely depended upon the molecular proportion of the components of the catalyst (Fig 1). Figure 2 shows the influence of the catalyst content on the

Some Chemical Properties of Phenyltitantriisopropylate and Its Catalytic Power in the Polymerization of Olefines SOV/2o-127-3-28/71

output of the polymer. Based upon the above investigation, the experts arrived at the following conclusion: titanoxychloride is the actual catalyst in the polymerization of the catalytic system $C_6H_5Ti(i\text{-}OC_3H_7)_3$. It is produced by several reactions which precede polymerization. Phenyl radicals do not take part in the mentioned process. This is confirmed by the i.-r. spectrum (Fig 3). There are 3 figures and 7 references, 1 of which is Soviet.

SUBMITTED: May 12, 1959

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5(3).

AUTHORS: Razuvayev, G. A., Corresponding Member, AS USSR, Petukhov, G. G., Zateyev, B. G. SOV/20-127-4-20/60

TITLE: An Investigation of the Reactions of Transfer of Phenyl Radicals

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 4, pp 803-804 (USSR)

ABSTRACT: On the basis of a previous article (Ref 1) the authors investigated here the decomposition of various compounds yielding phenyl radicals: (a) nitroso-azeto-anilide; (b) diphenyl iodonium iodide; (c) double salt of phenyl-diazonium with cyanine chloride. This occurred in a solution of benzene marked with C^{14} in the presence of metallic mercury. (a) This substance (Ref 2) is known to produce phenyl mercury chloride if it is solved in CCl_4. On the whole, reaction with benzene took place. The isolated diphenyl (1.5 g, yield 50%) consisted of phenyl radicals of the nitroso compound and of benzene. Nonetheless, partial interaction took place between the radicals and mercury. The phenyl mercury acetate obtained from this reaction was converted into chloride; it proved to be inactive after several recrystallizations, whereas diphenyl showed an activity of 373 pulses/min, i.e. 45%

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An Investigation of the Reactions of Transfer of Phenyl Radicals

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of the phenyl radicals out of benzene. The decomposition of nitroso-acetanilide over freshly reduced copper in a medium of benzene labelled with C^{14} did not effect a considerable variation in the isotopic composition of the diphenyl obtained. Similar results were obtained from (b). The resultant iodobenzene is also inactive. Hence, benzene as a solvent does not participate in the reaction. Phenyl mercury iodide is formed by diphenyl iodonium iodide and not by iodobenzene which results from the decomposition of the latter. This is also confirmed by the fact that under equal conditions no phenyl mercury iodide is produced from iodobenzene and mercury. (c) The decomposition of the double salt $(C_6H_5N_2)_2ZnCl_4$ at 30° in a medium of labelled benzene caused the formation of chlorobenzene as the main product (Table 1) which after careful purification was virtually inactive. Besides, a small quantity of diphenyl was produced. The composition of isotopes of the latter indicated that the phenyl radicals of benzene and phenyl diazonium had participated in its formation. To explain whether this process was accompanied by the formation of free radicals, the authors decomposed the

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double diazo salt in the presence of metallic mercury (Experiments 3 and 4, Table 1); but these experiments failed as no phenyl-mercury compounds could be obtained. The same applied to sodium amalgam which had been substituted for mercury (Experiment 4). Neither a mercury- nor a sodium amalgam addition affected the yields of chlorobenzene and diphenyl. Nor was this the case with metallic zinc and copper, which could not alter the decomposition of the double diazonium salt in benzene. (Experiments 5 and 6). Hence, formation of free phenyl radicals could not be found. There are 1 table and 3 Soviet references.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom Gosudarstvennom universitete im. N. I. Lobachevskogo (Scientific Institute of Chemistry of Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: May 13, 1959

5(2,3)

AUTHORS: Razuvayev, G. A., Corresponding Member, AS USSR, Grayevskiy, A. I. SOV/20-128-2-24/59

TITLE: On the Determination of Organoaluminum Compounds by the Indicator Method

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 2, pp 309-311 (USSR)

ABSTRACT: The compounds mentioned in the title are used as catalysts in the polymerization of ethylene, propylene and other α-olefines, generally in the form of diluted solutions (0.1-10%). There is no quick and simple method of analyzing such solutions. It was of interest to clarify of what kind is the interaction of the aluminum alkyls, -aryls, and their derivatives with indicators and organic bases. It might be assumed that titration is possible in the presence of the usual acidic-alkaline indicators. The compounds mentioned below were, for this purpose, dissolved in toluene rid of oxygen, and mixed with solutions of methyl violet in dichloroethane. It was found that the indicator, by addition of $Al(C_2H_5)_3$ or its halogen derivatives, turns from

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violet (alkaline form) into yellow or green (acid form). $Al(C_6H_5)_3$ (supplied by Ye. V. Mitrofanova) and $Al(C_4H_9)_3$ (supplied by A. F. Popov) had a similar effect on the indicator. When an excess of any organic base is added to these yellow or green solutions, they turn violet again. Compounds of type AlR_2OR and $AlR(OR)_2$ do not change the color of the indicator.

The neutral properties of these substances can probably be explained by the screening of the 3p-level of the aluminum by free electron doublets of the oxygen. The authors titrated the compounds mentioned in the title with some organic bases: butyl- and ethyl acetate, dimethyl aniline, ethyl ether, pyridine, etc while indicators were used. Such indicators were chosen which are well soluble in organic solvents, and produce a distinct color change in the equivalent point. As a rule, they contained amino groups: methyl violet, crystal violet, gentian violet, etc. Figure 1 shows (a,b,v,g) the titration curves of $Al(C_6H_5)_3$ and $Al(C_2H_5)_2Cl$, of $AlC_2H_5Cl_2$, of the sesquichloride, and of $Al(C_2H_5)_2Br$ by dimethyl aniline in toluene

in the presence of methyl violet. The results obtained allow the following conclusions: 1) The said curves remind of those of the titration of strong acids by strong bases. The aluminum alkyls and -aryls are rather strong aprotonic acids. 2) Dimethyl aniline reacts with these acids in a ratio of 1 : 1. 3) $Al(C_2H_5)_2Br$ and $AlC_2H_5Cl_2$ are very different from $Al(C_6H_5)_3$ and $Al(C_2H_5)_2Br$ with respect to their strength. 4) $Al(C_2H_5)_2Br$ behaves like a dibasic acid, which circumstance has not yet been explained satisfactorily. 5) When $Al(C_2H_5)_2Cl$ and $AlC_2H_5Cl_2$ are present at the same time, they can be determined separately. Table 1 reveals that there is a parallelism between the results obtained by the dilution method, and the electrochemical data. On this basis, the authors put the acids in the following order with respect to their strength: $Al(C_2H_5)_3 < Al(C_2H_5)_2Cl < Al(C_2H_5)_2Br < AlC_2H_5Cl_2$. There are 1 figure, 1 table, and 2 references.

SUBMITTED: June 6, 1959

RAZUVAYEV, Grigoriy Alekseyevich, laureat Leninskoy premii; LATYAYEVA, Viktoriya Nikolayevna, kand.khim.nauk; VAYNBOYM, I.B., red.; ATROSHCHENKO, L.Ye., tekhn.red.

[Free radicals in chemistry] Svobodnye radikaly v khimii. Moskva, Izd-vo "Znanie," 1960. 39 p. (Vsesoiuznoe obshchestvo po rasprostraneniiu politicheskikh i nauchnykh znanii. Ser.9, Fizika i khimiia, no.23). (MIRA 14:1)

1. Chlen-korrespondent AN SSSR (for Razuvayev).
(Radicals (Chemistry))

PHASE I BOOK EXPLOITATION SOV/4983

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii, SSSR, Moskva, 14-18 iyunya 1960 g; doklady i avtoreferaty. Sektsiya II. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18; Papers and Summaries) Section II. [Moscow, Izd-vo AN SSSR, 1960] 559 p. 5,500 copies printed.

Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry

Tech. Ed.: T.A. Prusakova.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high-molecular compounds.

COVERAGE: This is Section II of a multivolume work containing papers on macromolecular chemistry, The papers in this volume treat mainly the kinetics of various polymerization reactions initiated by different catalysts or induced by radiation. Among the research techniques discussed are electron paramagnetic resonance spectroscopy and light-scattering interpolation. There are summaries in English, French and Russian. No personalities are mentioned. References follow each article.

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S/081/61/000/024/031/086
B117/B147

AUTHORS: Razuvayev, G. A., Grayevskiy, A. I., Demin, O. I., Minsker K. S., Sukharev, Yu. G.

TITLE: Oxidation of triethyl aluminum and study of the catalytic properties of the oxidation products

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 24, 1961, 240, abstract 24Zh196 (Tr. po khimii i khim. tekhnol. (Gor'kiy), no. 3, 1960, 373 - 380)

TEXT: The oxidation of solutions of $Al(C_2H_5)_3$ (I) and its derivatives in n-heptane has been studied at various temperatures and concentrations. Reaction products were analyzed as to their content of peroxide compounds and their decomposition products. Peroxide compounds with an amount increasing with decreasing concentration of the solution and decreasing reaction temperature are very unstable. At 20°C they decompose in very weak solutions almost immediately to give oxy derivatives of I. The following oxidation pattern of I is proposed:

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Oxidation of triethyl ...

$I + O_2 \rightarrow [Al^-OO^+(C_2H_5)_3] \rightarrow (C_2H_5)_2AlOOC_2H_5 \rightarrow AlC_2H_5(OC_2H_5)_2$ (II);
$II + I \rightarrow 2Al(C_2H_5)_2OC_2H_5$ (III). The polymerizability of II and III in the case of α-olefins was studied on systems of I + II + III + $TiCl_4$. Oxidation products of I and of its derivatives are ordinary catalysts of the Ziegler type but much less reactive. When they are added to I, the quality of the resulting polymer is not deteriorated, but the catalytic activity of I and the molecular weight of the polymer are lowered. In order to eliminate the detrimental effect of the admixture, it is recommended that the total concentration of the $TiCl_4$/RAl catalyst and the ratio of C_2H_5 to Ti should be increased at the same time. [Abstracter's note: Complete translation.]

Card 2/2

RAZUVAYEV, G.A.; ZATEYEV, B.G.; PETUKHOV, G.G.

Mechanism of the reaction between benzoyl peroxide and benzene. Sbor. nauch. rab. Inst. fiz.-org. khim. AN BSSR no.8:41-43 '60. (MIRA 14:3)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N.I. Lobachevskogo.

(Benzoyl peroxide) (Benzene)

RAZUVAYEV, G.A.; LIKHTEROV, V.R.; ETLIS, V.S.

Decomposition of acetylcyclohexanesulfonyl peroxide in organic solvents. Sbor. nauch. rab. Inst. fiz.-org. khim. AN BSSR no.8:44-50 '60. (MIRA 14:3)

(Cyclohexanesulfonyl peroxide)

RAZUVAYEV, G.A.

Catalytic polmerization of propylene acted upon by titanium compounds. Sbor. nauch. rab. Inst. fiz.-org. khim. AN BSSR no.8:76-79 '60. (MIRA 14:3)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N.I. Lobachevskogo.
(Titanium organic compounds) (Polymerization) (Propene)

RAZUVAYEV, G.A.; TERMAN, L.M.

Radical reactions of percarbonates. Sbor. nauch. rab. Inst. fiz.-org. khim. AN BSSR no.51-57 '60. (MIRA 14:3)
(Peroxycarbonates) (Radicals(Chemistry))

81583

S/190/60/002/03/03/014
B020/B066

5.3831

AUTHORS: Razuvayev, G. A., Minsker, K. S., Fedoseyeva, G. T., Bykhovskiy, V. K.

TITLE: Effect of Polar Additions on the Stereospecific Polymerization of Propylene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 3, pp. 404-407

TEXT: The authors have recently shown that the addition of amines in the stereospecific polymerization and in the presence of a catalyst system (consisting of titanium chloride and triethyl aluminum) changes the degree of polymerization of polymers. The ratio of the fractions is not considerably influenced. The effect of other types of nucleophilic compounds containing an undivided electron pair that may interact both with the unoccupied 3-p level of the central Al atom in triethyl aluminum and with the d-shell of $TiCl_3$ is of special interest in this connection. It was presupposed that these compounds, like the amines

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(Ref. 1), exert an influence upon the ratio of the reaction of growth to the interruption of the chain. Representatives of the class of ethers (dioxane), sulfides (diphenyl sulfide), and of the heterocyclic compounds (pyridine, thianthrene) were selected. The results of experiments on the effect of these compounds on the stereospecific polymerization of propylene are given (Table). With an increasing ratio between addition and titanium chloride also the molecular weight of the polymer increases as much as on application of amines. The maximum molecular weight found in dioxane with a ratio of < 1 between addition and titanium chloride is to be explained by the presence of two electron donor atoms in its molecule. Dioxane and pyridine accelerated stereospecific polymerization, which had not been expected by the authors (Fig.). The authors outlined (Ref. 1) the possibility of the formation of complex compounds between $TiCl_3$ and aniline, dimethyl aniline, and triethyl aniline in the presence or absence of triethyl aluminum. This may also be compared with the effect of the increasing molecular weight of the resultant polymer on polymerization of the Ziegler type and in the presence of ether additions. T. A. Domracheva

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Effect of Polar Additions on the Stereospecific Polymerization of Propylene

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contributed to the experimental part. Mention is made of C. D. Nenițescu (Ref. 3), A. V. Topchiyev and co-workers (Refs. 4,5), V. Michovich and M. Mikhaylovich (Ref. 12), T. V. Talalayeva and K. A. Kocheshkov (Ref. 8). There are 1 figure, 1 table, and 19 references: 10 Soviet, 8 US, 2 German, and 1 Rumanian.

SUBMITTED: December 11, 1959

Card 3/3

86298

S/190/60/002/008/012/017
B004/B054

15.8100 2209

AUTHORS: Razuvayev, G. A., Minsker, K. S.

TITLE: The Role of Oxygen in the Polymerization of Vinylidene Chloride

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 8, pp. 1239-1245

TEXT: The present paper reports on a study of polymerization of vinylidene chloride in the presence of 95% molecular oxygen. Whereas in previous papers (Refs. 1,2) it was found that vinyl chloride reacted with O_2 only slowly and only in the presence of initiators (benzoyl peroxide, azoisobutyric acid dinitrile), vinylidene chloride reacted very easily with O_2 to form peroxides, the initiators having no influence on the reaction rate up to 30°C. Vinylidene chloride peroxides are sparingly soluble in their own monomers. Normal polymerization of vinylidene chloride only starts when the oxygen is consumed, the latter acting as inhibitor. Although no free HCl was found in the gaseous phase, the molar ratio Cl : -OO- rose from 1 to 4 during the reaction. The peroxide groups are

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probably decomposed. If HCl is formed, it remains dissolved in the liquid phase. If the monomer excess was removed in the air flow after the reaction with O_2, a solid substance was left which contained 1.49-11.2% of peroxide oxygen and exploded at a content of more than 7% of peroxide oxygen between 86 and 98°C. The composition of the vinylidene chloride peroxide varied so that its formula could only be determined approximately: $3C_2H_2Cl_2O_2$ - HCl loss. Peroxides with high oxygen content accelerated the polymerization of vinyl chloride. On heating in water, a fast hydrolysis occurred with HCl becoming free. The peroxide of vinylidene chloride poorly dissolves in organic solvents, best in dioxane. The action of amines or dimethyl formamide leads to explosion. The formation rate of the peroxide group during the induction period of polymerization of vinylidene chloride in the presence of air, as well as in the presence or absence of initiators, depends linearly on temperature. An activation energy E = 9.8 kcal/mole was found for the non-initiated oxidation, whereas E was 38.5 kcal/mole in the case of initiation by azoisobutyric acid dinitrile. The cause of this difference has not yet been found. -C(O)-O-, -O-O-, and C=C groups were detected with the aid of infrared spectra of the polymer. The authors thank A. M. Fisher for

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The Role of Oxygen in the Polymerization of Vinylidene Chloride

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taking the spectra. They arrived at the conclusion that oxygen deteriorated the quality and stability of plastics made of vinylidene chloride. There are 5 figures, 2 tables, and 7 references: 4 Soviet, 1 US, and 2 Japanese.

SUBMITTED: April 4, 1960

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87777
S/063/60/005/006/012/014
A051/A026

5 3100 2209, 1164, 1273

AUTHORS: Razuvayev, G.A., Vyazankin, N.S., Dergunov, Yu. I., Pinchuk, N.M.

TITLE: The Reaction Between Hexaethyldistannane and Organic Haloid Derivatives

PERIODICAL: Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva im. D.I. Mendeleyeva, 1960, Vol. 5, No. 6, pp. 707-708

TEXT: The authors have investigated the reactions of hexaethyldistannane with certain organic haloid derivatives in evacuated ampules at elevated temperatures. It has been shown on the example of bromine- and iodine-benzene, that halogene, bound to the benzene ring, is not detached by the hexaethyl-distannane, when heated to 180-190°C for a period of 20-30 hours. In all other cases it was found that the rate and direction of the reaction depends on the nature of the haloid derivative. The hexaethyldistannane was found to react easiest with triphenylchloromethane (4.5 hrs at 100°C) and with n-toluenesul-fochloride (13 hrs at 100°C). In the first case the reaction takes place with the formation of triethylstannous chloride (yield 61.7% of the theoretical), and triphenylmethyl radicals. The presence of the latter was proven by the electronic paramagnetic resonance method. Triethyl stannous chloride (yield

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90.8%) and n-tolyltriethylstannylsulfon were formed from the reaction with the n-toluenesulfochloride. Yield of the second-18.7%, melting point 91-92°C (from alcohol). The structure of the sulfon has been verified by a counter synthesis, carried out in a medium of absolute alcohol (for 3 hours, at 78°C) with a yield of 44.2% of the theoretical:
$n\text{-}CH_3C_6H_4SO_2Na + (C_2H_5)_3SnCl \longrightarrow NaCl + n\text{-}CH_3C_6H_4SO_2Sn(C_2H_5)_3$ (1).
Under more severe conditions (4 hours at 190-200°C) the hexaethyldistannane reacts with the benzene chloride. The formation of dibenzene (yield 35.4%) in addition to the triethylstannous chloride (yield 73.4%, proves that a reaction with a homologous separation of the σ - links takes place. It is assumed that this type of decomposition of the bonds is characteristic for the $(C_2H_5)Sn_2$ reaction with β-bromoethylbenzene, 1.4-dibromobutane, and 1.5-dibromopentane also, taking place at 200-210°C. In all these cases it was found that, in addition to the main process of triethylstannous bromide (yield 70.5, 72.5 and 82.4%, respectively) formation, the disproportionation of the hexaethyldistannane takes place also: $2(C_2H_5)_6Sn_2 \longrightarrow 3(C_2H_5)_4Sn + Sn$. (2). It is further assumed that reaction (2) is catalyzed by triethylstannous bromide in the

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reactions discussed here, based on previously made assumptions (Ref. 2, the author), that reaction (2) is a catalytic one, just as the disproportionation of the hexaethyldiplumbane is (Ref. 1-3, the author). This assumption was confirmed by the thermostatic action of the mixture hexaethyldistannane and triethylstannous chloride, at 200-210°C (10 hours, molar ratio 1:2). Reaction (2) takes place more energetically in the presence of 3 moles of dichloroethylstannate and 2 moles of hexaethyldistannane (for a period of 1 h , at 200°C). The formed tetraethylstannate reacts with the dichloroethylstannate, forming triethylstannous chloride: $2(C_2H_5)_6Sn_2 + 3(C_2H_5)_2SnCl_2 \rightarrow 6(C_2H_5)_3SnCl + Sn$. (3). It is stressed that equation (2) describes only the final result. The reaction mechanism is thought to be complex from the following indications: during the reaction intensive wine-colored, presumably high-molecular compounds are formed, decomposing toward the end of the process, the stannous chloride is thought to play an important role in equation (2), usually identified when conducting the disproportionation in an excess of dichloroethylstannate. It was established that the $SnCl_2$ can cause changes not only in the hexaethyldistannane, but also in the more stable tetraalkyl

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derivatives of the tin. The following reaction is given as an example of the thermostatic action of equimolar quantities of tetraethylstannate and $SnCl_2$ (for 10 hours at 230°C): $2(C_2H_5)_4Sn + 2SnCl_2 \rightarrow 2(C_2H_5)_3SnCl + (C_2H_5)_2SnCl_2 +$ + Sn. (4) also taking place with the formation of dark-red colored intermediary compounds. Another fact proving the complexity of the reaction is given as being the fact that catalytic quantities of $(C_2H_5)_3SnCl$ and $(C_2H_5)_2SnCl_2$ (2% of the weight of hexaethyldistannane) do not bring about its complete conversion according to equation (2). It is pointed out that the interaction of the hexaethyldiplumbane with an excess of triethyl lead chloride triethylstannous chloride or dichlorodiethylstannate, takes place quite differently. In this case the disproportionation reaction is completely suppressed by the complex oxidation- reduction process. In conclusion the authors state that investigations are still being continued in this field. There are 3 Soviet references.

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet im. N.I. Lobachevskogo (The Gor'kiy State University im. N.I. Lobachevskiy)

Card 4/4

5.3600, 5.3400

77515
SOV/79-30-2-64/78

AUTHORS: Razuvayev, G. A., Spasskaya, I. F., Etlis, V. S.

TITLE: Chlorination of Propylene Glycol

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 653-657 (USSR)

ABSTRACT: The chlorination of propylene glycol initiated by UV irradiation, acetyl cyclohexyisulfonyl peroxide, or azo-bis-isobutyronitrile gave a mixture consisting of 10-15% dichloropyruvic acid (I), 24-28% 1,1,3-trichloracetone (III), and 15-21% of an ester of dichloropyruvic acid and propylene chlorohydrin (II). The formation of the above compounds can be explained by the oxidation and chlorination reactions accompanied by esterification. Carbonyl compounds (pyruvic aldehyde, acetylcarbinol, and hydroxypropanal) are formed first. Hydrogen chloride formed in the chlorination reacts with propylene glycol and gives chiefly 1-chloropropanol-2 and water. The former is oxidized by

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chlorine to 1,1,3-trichloroacetone, and the simultaneous oxidation and chlorination of pyruvic aldehyde give dichloropyruvic acid. The oxidation of both OH groups in propylene glycol competes here with the reaction of propylene glycol and HCl. It can be deduced from the above that the presence of water in the starting propylene glycol assists the oxidation and should improve the yield of I. Actually, the chlorination of 50% and 25% aqueous mixtures of propylene glycol gave I in 40% yield as compared with 10-15% yield of chlorination of anhydrous propylene glycol. The chlorination of 34% aqueous solution of pyruvic aldehyde under UV irradiation gave I in 81% yield. Mercury quartz lamp PRK-2 was used in the experiments. Time of chlorination was 60-80 hr. There are 8 references, 1 U.K., 1 Czechoslovak, 3 German, 3 Soviet. The U.K. reference is: Brit. Pat. 354798

SUBMITTED: February 25, 1959

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S/079/60/030/04/60/080
B001/B011

5.3700B

AUTHORS: Razuvayev, G. A., Vyazankin, N. S., Dergunov, Yu. I.

TITLE: Reaction of Hexaethyl Diplumbane With Alkyl Halides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp. 1310-1316

TEXT: The reactions of the compounds of type R_6Pb_2 with alkyl halides are still insufficiently investigated. Paper of Ref. 3 along with some others allows the conclusion that a mixture of compounds PbX_2, R_2PbX_2, and R_3PbX results as the end product of the reaction, with R being an organic radical and X a halogen. Moreover, one must in certain cases add compounds of the type R_4Pb to the reaction products (at least according to the patent of Ref. 4). The following was ascertained: 1) In the case of reaction of equimolecular amounts of alkyl halide and hexaethyl diplumbane several reactions occur giving rise to many different products. 2) In the presence of catalytic amounts of alkyl halides there occurs a strong decrease in stability of hexaethyl diplumbane and its disproportionation according to scheme (I)

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Reaction of Hexaethyl Diplumbane With Alkyl Halides

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$2(C_2H_5)_6Pb_2 \longrightarrow 3(C_2H_5)_4Pb + Pb$. Investigation results are given in Table 1. They include reactions of hexaethyl diplumbane with equimolecular amounts of ethyl bromide, 1,2-dibromo ethane and 1,2-dibromo propane. Such reactions yield tetraethyl lead, lead bromide, triethyl lead bromide, dibromo diethyl lead and metallic lead. A reaction scheme was suggested. Furthermore, the authors investigated the reaction of hexaethyl distannane with 1,2-dibromo ethane, with triethyl tin bromide and ethylene resulting as the main products. It was found that, apart from the thermal decomposition reaction $(C_2H_5)_6Pb_2 \longrightarrow (C_2H_5)_4Pb + Pb + 2C_2H_5$, also a disproportionation of hexaethyl diplumbane takes place: $2(C_2H_5)_6Pb_2 \longrightarrow 3(C_2H_5)_4Pb + Pb$, which is brought about by the aid of catalysts. The catalysts used were metal chlorides of type $AlCl_3$, mixed organometallic compounds and products reacting with hexaethyl diplumbane under formation of the above catalysts (e.g. dibromo ethane). The authors refer to a paper by Ya. K. Syrkin (Ref. 5). There are 2 tables and 12 references, 6 of which are Soviet.

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet (Gor'kiy State University)
SUBMITTED: May 7, 1959

Card 2/2

85393
S/079/60/030/006/027/033/XX
B001/B055

2209, 1273, 1312

AUTHORS: Razuvayev, G. A., Mitrofanova, Ye. V., and Petukhov, G. G.

TITLE: Some Reactions of Triphenyl Aluminum

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 6, pp. 1996 - 2002

TEXT: Systems containing alkyl compounds of aluminum and halogen compounds of titanium are recently being used as catalysts in the polymerization of α olefins. The mechanism of this type of polymerization is still unclear. A radical mechanism was suggested in Refs. 1-7. The authors of the present paper believed that the formation of free radicals in these systems can be determined comparatively simply by introducing a substance like triphenyl aluminum into them, since it is known that phenyl radicals in solutions are detectable (Refs. 8,9). Triphenyl aluminum, in a system containing titanium tetrachloride, has already been used as a catalyst for the stereospecific polymerization of α olefins (Refs. 10,11). It was of great interest in this connection,

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Some Reactions of Triphenyl Aluminum

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To study the reaction of triphenyl aluminum with $TiCl_4$ in tagged benzene, and also its reaction with metallic Hg and $TiCl_4$. To begin with, it was found that no exchange reaction of phenyl radicals takes place between triphenyl aluminum and tagged benzene (Ref.12); the product formed contained no deuterium (Table 1). Reaction of triphenyl aluminum and $TiCl_4$ in deuterated benzene gave a diphenyl in 25% yield referred to three phenyl groups of triphenyl aluminum. In all experiments, the diphenyl contained deuterium. The deuterium content was a measure for the degree of hydrogen exchange (Table 2). The formation of deuterated diphenyl is best illustrated by the following Scheme:

$$Ph_3Al + 2TiCl_4 \longrightarrow \left[Ph_3Al \cdot 2TiCl_4\right] \rightarrow PhAlCl_2 + \left[2PhTiCl_3\right];$$

$$\left[2PhTiCl_3\right] \longrightarrow Ph_2 + 2TiCl_3 .$$

Thus, the reaction carried out in various solvents gives diphenyl without intermediate formation of free phenyl radicals. This is shown by the absence of a "stepwise exchange" (i.e., by the absence of a reaction

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between free phenyl radicals and the tagged solvent, benzene, and by the absence of a reaction of phenyl with metallic mercury when the reaction is carried out in the presence of the latter metal. The oxidation of triphenyl aluminum solutions with oxygen follows a radical mechanism. This is performed by the use of triphenyl aluminum and benzene, both tagged with C^{14}. It was shown that the reaction products (diphenyl and phenol) are obtained from both phenyl radicals of triphenyl aluminum and the solvent benzene. The authors thank B. A. Redoshkin for carrying out one of the experiments. They mention A. N. Nesmeyanov and K. A. Kocheshkov. There are 4 tables and 20 references: 10 Soviet, 3 US, 4 German, and 3 Rumanian.

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet (Gor'kiy State University)

SUBMITTED: May 18, 1959

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85394

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B001/B055

53610 Khr. 2209

AUTHORS: Svetozarskiy, S. V., Razuvayev, G. A., Zil'berman, Ye.N., and Volkov, G. S.

TITLE: Reactions in Spontaneous Condensation of Cyclic Ketones and Their Condensation With Ammonia

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 6, pp. 2042 - 2047

TEXT: Basing on Refs. 1-6, the authors show in the present investigation that by spontaneous condensation of cyclopentanone under known conditions, one obtains the ketones (the bicyclic ketone 2-cyclopentylidene cyclopentanone and tricyclic ketone 2,5-dicyclopentylidene cyclopentanone) described in Refs. 7,8. In this case, the initially formed dihydroxy ketone is evidently unstable and readily splits off two molecules of water giving the unsaturated ketone (Scheme). By spontaneous condensation of 4- and 3-methyl cyclohexanone under ordinary conditions, tricyclic products were obtained (2-[2-(1-hydroxy-4-methyl-cyclohexyl)-1-hydroxy-4-methyl-cyclohexyl]-4-methyl cyclohexanone (I)

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Reactions in Spontaneous Condensation of Cyclic Ketones and Their Condensation With Ammonia

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and 2 [2-(1-hydroxy-5-methyl-cyclohexyl)-1-hydroxy-5-methyl-cyclohexyl] -5-methyl cyclohexanone (II)). By splitting off two molecules of water from these dihydroxy ketones, the α,β-δ,ε-unsaturated ketones (III) and (IV) were formed. At elevated temperatures, compounds (III) and (IV) form one and the same hydrocarbon, 2,6,10-trimethyl-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro triphenylene (V). Condensation of 4- and 3-methyl cyclohexanones with ammonia in the presence of calcium and ammonium chlorides gave substituted 2,3,4,5-tetrahydro-pyrimidines, compounds (VI) and (VII). The following β-amino ketones could be isolated from the hydrolysis products of the latter two substances: 2-(4-methyl-1-amino-cyclohexyl)-4-methyl cyclohexanone (VIII) and 2-(3-methyl-1-amino-cyclohexyl)-5-methyl cyclohexanone (IX). Thus, it is seen that cyclopentanone, cycloheptanone, cyclohexanone and its monomethyl-substituted isomers behave differently in spontaneous condensation and ordinary condensation with ammonia. The most reactive of the ketones listed are cyclohexanone and 4-methyl cyclohexanone. There are 8 references: 3 Soviet, 3 German, and 2 US.

SUBMITTED: June 23, 1959

Card 2/2

S/079/60/030/007/037/039/XX
B001/B066

AUTHORS: Razuvayev, G. A. and Terman, L. M.

TITLE: Radical Reactions of Percarbonates. I. Thermal Decomposition of Dibenzyl- and Dicyclohexyl-peroxy-dicarbonates in Benzene and Isopropyl Alcohol

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2387-2393

TEXT: Following the papers of Refs. 1-4 the authors report the results of their investigation of the decomposition mentioned above. It was found that the decomposition kinetics of these carbonates in benzene at 45°, 50°, 55°, 60°C (± 0.05°) and at a peroxide concentration of 0.075 mole/l can be expressed by a first-order equation as far as the peroxide reaction is concerned. The numerical values of the rate constant for each individual case were determined from the slope of the straight line $\log(c_0/c) = f(t)$ (Diagrams 1 and 2, where c_0 is the initial peroxide concentration, and c its concentration after the time t). The experimental points lie near the straight line, which indicates that a first-order reaction with respect to the peroxide takes place in both cases. The activation energy of per-

Radical Reactions of Percarbonates I. Thermal Decomposition of Dibenzyl- and Dicyclohexyl-peroxy-dicarbonates in Benzene and Isopropyl Alcohol

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oxide decomposition in benzene solution was calculated from the slope of the straight line log K = f(1/T) (Diagram 3, straight lines 1 and 2). The numerical values of the rate constants of decomposition of the percarbonates and those of the activation energy are given in Table 1. Radicals of the RO•RO• type were formed by thermal decomposition of dissolved percarbonates. The radicals are able to split hydrogen from the solvent (decomposition in isopropyl alcohol) or to disproportionate it (decomposition in benzene). The decrease of percarbonate concentration during their decomposition in the solvents obeys the kinetic law of first-order reactions, the activation energy of the process being dependent on the nature of the solvent. When the percarbonates in decompose solvents, the peroxide molecule is cleft on the O-O bond, followed by evolution of CO_2 and formation of RO• radicals. There are 4 figures, 1 table, and 14 references: 3 Soviet, 8 US, 1 German, and 2 French.

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet (Gor'kiy State University)

SUBMITTED: August 31, 1959

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85713

S/079/60/030/008/010/012/XX
B001/B066

5.3700 2209, 1153, 1273

AUTHORS: Razuvayev, G. A., Vyazankin, N. S., and Shchepetkova, O. A.

TITLE: Thermal Decomposition of Lead Tetraethyl, Hexaethyl-diplumbane, and Their Analogs. III. Reactions of the Homolytic Decomposition of Hexaethyl-diplumbane and Hexaethyl-distannane

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 8, pp. 2498-2506

TEXT: The authors pointed out in Refs. 1,2 that the thermal decomposition of liquid lead tetraethyl takes place through the formation of less ethylated compounds, such as hexaethyl-diplumbane and lead diethyl:

$(C_2H_5)_4Pb \longrightarrow (C_2H_5)_6Pb_2 \longrightarrow (C_2H_5)_2Pb \longrightarrow Pb$. It is however, very doubtful whether a continuous homolytic cleavage of the σ-bonds takes place in this course of reaction. In order to obtain a complete and well-founded scheme of decomposition, it will be necessary to know the reactions of the homolytic cleavage of lead tetraethyl and of its intermediates formed

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Thermal Decomposition of Lead Tetraethyl, Hexaethyl-diplumbane, and Their Analogs III. Reactions of the Homolytic Decomposition of Hexaethyl-diplumbane and Hexaethyl-distannane

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during decomposition, as well as the role played by free radicals in these conversions. The investigation of the homolytic cleavage of hexaethyl-diplumbane and its organotin analog (hexaethyl-distannane) is, therefore, highly important. In the smooth reaction of hexaethyl-distannane with dibromo ethane giving rise to tin triethyl-bromide and ethylene (Ref. 3), the reactants had been assumed to form a cyclic transition complex which split in a homopolar way. To study the possible appearance of such ring complexes also in other reactions of hexaethyl-distannane, it was allowed to react with compounds in a benzene solution, which readily decompose into radicals. Hexaethyl-distannane and diplumbane were found to decompose homolytically at the metal-metal bond when treated with labile organic compounds in a benzene solution at a normal temperature. These labile compounds included benzoyl peroxide, acetyl-benzoyl peroxide, cyclohexyl percarbonate, azo-isobutyric acid dinitrile, nitroso-acetanilide, and lead tetraacetate. The reactions are assumed to proceed through the formation

Thermal Decomposition of Lead Tetraethyl, Hexaethyl-diplumbane, and Their Analogs. III. Reactions of the Homolytic Decomposition of Hexaethyl-diplumbane and Hexaethyl-distannane

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of homolytically decomposing ring complexes. The solvent participates in the reaction of hexaethyl-stannane with the above compounds in CCl_4, whereby, in addition to other reaction products, also tin triethyl chloride results. The formation of the latter is initiated by the reaction of CCl_4 with the labile compound. Nitroso-acetanilide reacts at a normal temperature with CCl_4, bromo-ethyl, benzyl chloride, and the methyl ester of chloro-acetic acid to give phenyl diazonium chloride and bromide, acetic acid, and trace amounts of diphenyl. There are 13 references: 7 Soviet, 4 US, and 2 British.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete (Scientific Research Institute of Chemistry at Gor'kiy State University)

SUBMITTED: July 21, 1959

Card 3/3

87538

5 3400

S/079/60/030/012/024/027
B001/B064

AUTHORS: Razuvayev, G. A. and Boguslavskaya, L. S.

TITLE: Synthesis by Means of Free Hydroxyl Radicals. I. Oxidizing Dimerization of Aliphatic Ethers and Esters

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp. 4094-4099

TEXT: In consideration of the papers (Refs. 1-10) the authors investigated the dimerization of aliphatic ethers and esters, as this method permits synthesizing the ethers and esters of glycols with a long carbon atom chain as well as the esters of dibasic carboxylic acids. Moreover, the study of the structure of the dimerization products of these ethers and esters is of interest with respect to the reactivity of the hydroxyl radicals. It was shown that also substances of the inertness of ether yield products of oxidizing dimerization. Thus, it was possible to obtain a dimer from the reaction of diisopropyl ether with Fenton's reagent (Ref. 1) (approximately 3% calculated with respect to the hydrogen peroxide used) (Table). The diethyl ether oxidizes vigorously to acetaldehyde and furthermore partially to acetic acid, but it was not

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Synthesis by Means of Free Hydroxyl Radicals. I. Oxidizing Dimerization of Aliphatic Ethers and Esters

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possible to separate the dimer in pure state from the mixture of the products with high boiling point. Two compatible reactions occur when reacting the esters, especially the acetates, with Fenton's reagent: the dimerization of the organic radicals and oxidation under the formation of carbonyl compounds. By the amount of the separated dimer and the acetic acid, it is possible to evaluate the relative amounts of the dimerizing and oxidizing monomeric ester. The longer the carbon chain of the alcohol radical grows the more reduces the relative amount of the oxidizing monomer is reduced, while the yield of dimerization products increases considerably. Their yield obtained from n-butyl acetate and isoamyl formate is 12%. The dimerization of the esters is accompanied by the formation of tetramers and polymers. 7.6% of the dimer, 2.9% of the tetramer, and 2% polymers result from the reaction of n-butyl acetate with hydroxyl radicals. Simultaneously with the oxidation of the monomeric esters with primary alcohols the respective aldehydes are formed. Thus, n-butyraldehyde is formed from n-butyl acetate, and isovaleraldehyde from isoamyl acetate. The study on synthesis and structure of the dimers obtained is continued. There are

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Synthesis by Means of Free Hydroxyl Radicals. I. Oxidizing Dimerization of Aliphatic Ethers and Esters

87538
S/079/60/030/012/024/027
B001/B064

1 table and 15 references: 3 Soviet, 6 US, 1 German, and 5 British.

SUBMITTED: January 28, 1960

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S/079/60/030/012/025/027
B001/B064

AUTHORS: Razuvayev, G. A., Vyazankin, N. S., and Vyshinskiy, N. N.

TITLE: Thermal Decomposition of Lead Tetraethyl, Hexaethyl Diplumbane and Their Analogues. IV. Effect of Precipitating Lead, the Walls of the Vessel and Other Factors Upon the Decomposition Process

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp.4099-4104

TEXT: The authors showed previously (Ref.1) that the thermal decomposition of lead tetraethyl in the liquid phase is a complex chain process proceeding under the formation of less ethylated compounds, hexaethyl diplumbane and lead diethyl:
$(C_2H_5)_4Pb \longrightarrow (C_2H_5)_6Pb_2 \longrightarrow (C_2H_5)_2Pb \longrightarrow Pb$ (I). The formation of a solid phase, metallic lead, is characteristic of this reaction. Previous findings on the decomposition kinetics of binary mixtures of lead tetraethyl and hexaethyl diplumbane (Ref.6) were used to study the role played by this metal in the complicated thermal decomposition processes. Fig.1 shows that the concentration of hexaethyl diplumbane reaches a limit

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Thermal Decomposition of Lead Tetraethyl, Hexaethyl Diplumbane and Their Analogues. IV. Effect of Precipitating Lead, the Walls of the Vessel and Other Factors Upon the Decomposition Process

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B001/B064

characteristic of the given temperatures in the decomposition of pure lead tetraethyl, and that it drops subsequently. It was expected in the decomposition of a specially prepared mixture consisting of $(C_2H_5)_4Pb$ and $(C_2H_5)_6Pb_2$, with a concentration of the second component being close to the limit concentration, that the kinetic curve consist of the descending branch only. Also in this case, however, the concentration of hexaethyl diplumbane increases. These findings are in favor of the fact that lead acts as a catalyst in the splitting of the decomposition intermediates, since in its absence a concentration of hexaethyl diplumbane is observed, and in the presence of considerable amounts of highly disperse metal the $(C_2H_5)_6Pb_2$ concentration is reduced. It was found that in the decomposition of lead tetraethyl the final product, the highly disperse metallic lead, catalyzes the decomposition intermediates (hexaethyl diplumbane and lead diethyl), so that this thermal decomposition may be regarded as an autocatalytic process. The wall of the vessel has no essential effect upon the decomposition process of lead

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tetraethyl and hexaethyl diplumbane. In the presence of atmospheric oxygen the oxidation of lead tetraethyl suppresses the thermal decomposition reaction completely. Traces of atmospheric oxygen and products of the incomplete oxidation of lead tetraethyl inhibit the thermal decomposition process considerably. Stronger inhibitors of the thermal decomposition reaction of lead tetraethyl are small quantities of dibromo ethane and other alkyl halides. Fig.3 shows the effect of atmospheric oxygen upon the decomposition of lead tetraethyl at $135\pm0.3^{\circ}C$. Table 1 shows that the separation of lead from the reaction mixture leads to a concentration of the decomposition intermediate product of hexaethyl diplumbane. Yu. I. Dergunov took part in some of the experiments. There are 3 figures, 3 tables, and 7 references: 5 Soviet, 1 American, and 1 German.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete (Scientific Research Institute of Chemistry of Gor'kiy State University)

SUBMITTED: January 8, 1960

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SOV/20-130-1-28/69

5(3)

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR, Vasileyskaya, N. S., Oleynik, E. P.

TITLE: Ways of Hexachloroethane Formation in Photoreactions Between Carbon Tetrachloride and Alcohols

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 130, Nr 1, pp 102-104 (USSR)

ABSTRACT: K. Pfordte (Ref 6) indicated a scheme for the process mentioned in the title (3). He assumed the formation of C_2Cl_6 to be a consequence of the dimerization of CCl_3 radicals. The authors, however, consider another way of C_2Cl_6 formation possible. At first, the same process occurring in the thermal action may occur in the photoreaction (Equation 1). But then, $CHCl_3$ reacts with CCl_4 according to the formula $CHCl_3+CCl_4 \xrightarrow{h\nu} C_2Cl_6+HCl$ (4). This happens really when irradiating the mixture of 46.5 g of CCl_4 and 17.9 g of $CHCl_3$ by means of the mercury-quartz lamp of type PRK-2. 4.0 g of C_2Cl_6 are formed within 1 month.

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Ways of Hexachloroethane Formation in Photoreactions Between Carbon Tetrachloride and Alcohol

To solve this problem, the authors used the reaction [illegible] with metals (3) during which C_2Cl_6 is formed. [illegible] (5.0 ml, activity 900 imp/min) was heated with 12.9 ml [illegible] for 10 h in the presence of skeleton nickel in nitrogen atmospheres up to 80°. In this case, the primary formation reaction of the CCl_3 radicals can only be the interaction between CCl_4 and Ni: $CCl_4 + \frac{1}{2}Ni \longrightarrow CCl_3 + \frac{1}{2}NiCl_2$.

The C_2Cl_6 (6 imp/min) and CCl_4 (3 imp/min) isolated from the reaction mixture were not active. Therefore, the reactions (5) and (6) did not take place here. It was investigated separately whether the reaction (6) (may take place) [illegible] radicals takes place. For this purpose, a mixture of 5.0 ml of CCl_4 and 5.0 ml of CH_3I (activity 772 imp/min) was [illegible] under nitrogen with UV rays for 17 h. The CH_3I isolated was not active (2 imp/min) whereas the resulting CH_3I [illegible] 310 imp/min

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Therefore, reactio [illegible] did not take place [illegible] (5) and (6, which [illegible] [illegible] clarify the formation mechanism of [illegible]$_6$ in the [illegible] reaction were [illegible] here. By UV irradiation (for [illegible] nitrogen) of 15.5 [illegible], 2.2 ml [illegible] I_2 (9[illegible] [illegible] 15.0 ml CH_3OH, the authors found that the CCl_3 [illegible] tear away the H from the alcohol in the reaction [illegible] $CHCl_3$ is formed in the reaction (3). [illegible] [illegible] dimerization of CCl_3 radicals which develop in the [illegible] of CCl_4. According to the authors' opinion, no hydrogen [illegible] takes place in the photoreactions by the [illegible] reaction (6) occurs [illegible] to the rather considerable [illegible] energy (Ref 8). There are 8 references, 2 of which [illegible]

ASSOCIATION: Gor'kovskiy gosudarstvennyy universitet im. [illegible] (Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: September 15, 19[illegible]

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5.3200 (A)

SOV/20-130-2-25/69

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR, Zateyev, B. G., ~~Petukhov, G.~~ G.

TITLE: By-products in the Reaction of Benzoyl Peroxide with Benzene

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 2, pp 336 - 337 (USSR)

ABSTRACT: In a previous paper (Ref 3), the authors proved a discrepancy between the computed and established isotope composition of diphenyl and quaterphenyl formed as by-products in the reaction mentioned in the title. Benzene and benzoyl peroxide (BP) marked with C^{14} were used for this experiment. Another experiment made under the conditions of reference 1 showed that 41% of phenyl radicals from the benzene are contained in the resulting diphenyl instead of the 50% computed. This value lies near the data obtained previously (Ref 3), as well as those by R. I. Milyutinskaya, Kh. S. Bagdasar'yan and Ye. A. Izrailevich (Ref 4). If it is assumed that the phenylation reaction proceeds further, and quaterphenyl develops from the terphenyl, the quaterphenyl

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must contain a phenyl ring from the benzene and 3 rings from the BP. Its isotope composition, however, diverges considerably. It was shown by experiments that 2 phenyl rings each from the benzene and from the BP are contained in the quaterphenyl. Therefore, another formation source of quaterphenyl must necessarily exist. To check this assumption, the authors added diphenyl and terphenyl to the reaction mixture benzene + BP. Inactive diphenyl was added to the benzene solution of marked BP (Experiment Nr 3). If diphenyl is produced from quaterphenyl, this addition should considerably reduce the activity of the quaterphenyl. The experiment, however, showed practically unchanged activity. Very similar results were obtained by addition of active diphenyl to a reaction mixture of inactive components (Experiment Nr 4). The isolated quaterphenyl contained no C^{14}. As in experiment Nr 4, inactive quaterphenyl was obtained by BP decomposition in benzene in the presence of the marked terphenyl added (Experiment Nr 5). In the interaction of BP with marked diphenyl under the conditions of reference 2, the isolated terphenyl correspond - with

respect to the isotope composition - to a terphenyl which contains a benzene ring from the BP per 1 molecule of diphenyl; the quaterphenyl - 2 BP rings per 1 molecule of diphenyl (Experiment Nr 6). On the basis of the paper by D. F. Tar and R. A. Long (Ref 5), the authors give a scheme for the total course of the BP reaction with benzene (considering the reaction in marked benzene). Accordingly, the quaterphenyl must develop due to the dehydrogenation in the reaction of the BP or the free radicals of tetrahydrodiphenyl. The isotope composition of the latter corresponds to the computation made on the basis of the scheme suggested. There are 1 table and 5 references, 2 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N. I. Lobachevskogo (Scientific Research Institute of Chemistry, Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: September 21, 1959

S/020/60/131/04/037/073
B011/B017

AUTHORS: Razuvayev, G. A., Corresponding Member, AS USSR, Zil'berman, Ye. I., Svetozarskiy, S. V.

TITLE: Production of the Hexacyclic Product of Autocondensation of Cyclohexanone

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 850-852 (USSR)

TEXT: As is known, 2-cyclohexylidenecyclohexanone is formed on storing a mixture of equal amounts of cyclohexanone and 60% aqueous H_2SO_4 (Ref 2) for 24 hours. The authors wanted to investigate the behavior of cyclohexanone in the presence of a more concentrated H_2SO_4. In their paper, they proved that a solid product with the empirical formula $C_{36}H_{52}O_2$ (Table 1) is formed by the reaction of cyclohexanone with methanolic H_2SO_4 (I). Furthermore, it was found that in the presence of methanol, n-butanol, or water and concentrated H_2SO_4 (Experiments 1, 2 and 3) always the same condensation product of cyclohexanone $C_{36}H_{52}O_2$ is formed. If the solvent does not participate in its formation, the mentioned product is a result of autocondensation of cyclohexanone. $C_{36}H_{52}O_2$ was also obtained in a low yield (1%) in the autocondensation of cyclohexanone into dodecahydro-1,2,3,4,5,6,7,8,9,10,11,12-triphenylene (Ref 3) (Experiment 4). Furthermore,

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Production of the Hexacyclic Product of Auto-condensation of Cyclohexanone

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it was found that 2-cyclohexylidenecyclohexanone is also transformed into $C_{36}H_{52}O_2$ (Experiment 6) in the presence of methanolic H_2SO_4. In the synthesis of 2-cyclohexylidenecyclohexanone, also (I) is formed besides the final product if the experiment is carried out for a longer period. On the other hand, some tricyclic autocondensation products of cyclohexanone do not produce substance (I) in the reaction with methanolic H_2SO_4. For this reason, the authors assume that the autocondensation of cyclohexanone into (I) passes the stage of formation of 2-cyclohexylidenecyclohexanone (1), (2). In experiments 1-3 and 6, dodecahydrotriphenylene was obtained as a by-product. In experiment 6, this may be explained by the reaction of a reversible aldol condensation (Refs 4-6). On heating with dilute aqueous acid and alkaline solutions until the boiling point is attained, product (I) is not hydrolyzed at atmospheric pressure. By boiling with concentrated HNO_3 (I) is oxidized to give adipinic acid. On heating to 250°, a water molecule is cleft off from (I), and $C_{36}H_{50}O$ is formed. Under ordinary conditions, in the presence of platinum oxide, (I) adds no hydrogen on catalytic hydrogenation, and the usual derivatives of carbonyl compounds are not obtained. (I) cannot contain any tertiary alcohol groups. Figure 1 shows

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Production of the Hexacyclic Product of Auto-condensation of Cyclohexanone

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B011/B017

the UV absorption spectrum. On the basis of the results obtained, the authors regard (I) as a hexacyclic diketone which contains 3 double bonds. 2 of them are conjugated with carbonyl groups whereas the third one is isolated. There are 1 figure, 1 table, and 10 references, 3 of which are Soviet.

SUBMITTED: December 25, 1959

Card 3/3

80487
S/020/60/132/02/33/067
B011/B002

53700(B)

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR, Vyazankin, N. S., Dergunov, Yu. I., D'yachkovskaya, O. S.

TITLE: Some Cases of Reactions for the Redistribution of Radicals in Organic Lead, Tin, and Silicon Compounds

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 2, pp. 364-366

TEXT: Heating of an asymmetric organometallic compound of type $R_3R'Pb$ with catalytic amounts of aluminum chloride, causes the redistribution of the radicals (Ref. 1). A dynamic equilibrium, and a mixture of all possible combinations of tetraalkyl derivatives of the concerned metal develop. The authors intended to investigate such cases of the above reaction in which the equilibrium is disturbed, thus causing a clear deviation of the interrelations between the reaction products from those occurring in general. The authors found out that hexaethyl dimetals are asymmetric, as for instance $(C_2H_5)_3SnR$, R being $(C_2H_5)_3Sn$. Assuming that the two radicals readily take part in their redistribution, the following mixture necessarily must develop (according to publications):

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Some Cases of Reactions for the Redistribution of Radicals in Organic Lead, Tin, and Silicon Compounds

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$(C_2H_5)_4Sn$ (I), $(C_2H_5)_3SnR$ (II), $(C_2H_5)_2SnR_2$ (III), $C_2H_5SnR_3$ (IV), and SnR_4 (V). However, there will be no equilibrium in the developing mixture since (III), (IV), and (V) are no "symmetrical" compounds. Theoretically it is therefore probable that (III) - (V) will enter into side reactions during the redistribution of radicals, and besides tetraethyl tin will develop a series of substances with chains of metal atoms still longer and more ramified. Due to the decomposition of molecules, there will be no equilibrium in the mixture (I) - (V). In agreement with the above theory, the authors found out that 2-3 weight% of aluminum chloride or other catalysts of the radical redistribution, rapidly reduce the stability of hexaethyl diplumbane and hexaethyl distannane, also altering its decomposition mechanism (equations (B) and (V)). It was spectroscopically proven however, that the decomposition of these two compounds takes place according to equation (B) developing an intermediate product of diethyl lead, and diethyl tin respectively. During the disproportionation of hexaethyl distannane (but not of hexaethyl diplumbane) however, highly-molecular intermediate products develop between 70°-75° under the influence of $AlCl_3$. This is in agreement with the above-mentioned reaction mechanism. In this case the equilibrium is disturbed by the participation of reaction products in

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Some Cases of Reactions for the Redistribution of Radicals in Organic Lead, Tin, and Silicon Compounds

side processes. This causes the formation of unstable products. The authors give further examples of publications on their statement (Refs. 3-8). The reaction between isopropylchloride and tetraethyl lead was not successful. Table 1 gives a summary of the authors' experiments. There are 1 table and 8 references, 2 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N. I. Lobachevskogo (Scientific Research Institute of Chemistry of the Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: February 15, 1960

Card 3/3

83901
S/020/60/134/003/014/020
B016/B054

5.3700

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR,
Latyayeva, V. N., and Vyshinskaya, L. I.

TITLE: Some Reactions of Bis-cyclopentadienyl-diphenyl Titanium

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 3,
pp. 612-614

TEXT: The authors compare some chemical properties of $(C_5H_5)_2TiAr_2$ with those of other organometallic compounds (Ar = aryl radical). To compare reactivity, they applied the exchange reaction radical - halogen for $(C_5H_5)_2TiCl_2$ and $(C_6H_5)_2Hg$ on the one hand, and for $(C_5H_5)_2Ti(C_6H_5)_2$ and $HgCl_2$ on the other. From a boiling solution of the components in benzene or methylene chloride, they isolated a) about 20% of the expected phenyl mercury chloride from benzene, and b) nearly the theoretical yield from methylene chloride. The reaction with sublimate was carried out in CCl_4 or in benzene at 80°C. The main products obtained were: bis-

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Some Reactions of Bis-cyclopentadienyl-diphenyl Titanium

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cyclopentadienyl-titanium dichloride and phenyl mercury chloride (1 : 2). The authors conclude from this ratio that in CCl_4 mainly (at about 70%) an exchange reaction takes place between bis-cyclopentadienyl-diphenyl titanium and the sublimate according to equation (2). In benzene solutions, the bis-cyclopentadienyl-titanium dichloride yield decreased to 24% while up to 90% of phenyl mercury chloride was formed. Further, chloro benzene, diphenyl, and calomel were isolated from the CCl_4 medium. Phenol also formed in the presence of atmospheric oxygen. The formation of these by-products is explained by a parallel reaction of the initial organo-titanium compound with the solvent. For this reason, the authors carried out the dissociation reactions of $(C_5H_5)_2Ti(C_6H_5)_2$ in different solvents.

With the exclusion of air, the original yellow color of the solution changed to dark green due to heating. The latter color corresponds to the paramagnetic form of bis-cyclopentadiene titanium (Ref. 4). The formation of chloro benzene and small amounts of diphenyl in a CCl_4 medium is known (Ref. 5). The authors assumed an original homolysis of the $Ti-C_6H_5$ bond and the formation of a free phenyl radical; to check this assumption they allowed $(C_5H_5)_2Ti(C_6H_5)_2$ to react with methyl- and isopropyl alcohol,

Some Reactions of Bis-cyclopentadienyl-diphenyl Titanium

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B016/B054

as well as with chloroform. On the basis of the results, the authors assume the following reaction mechanism: the initial titanium compound decomposes when heated or subjected to ultraviolet radiation, along with the separation of the phenyl radical and the formation of paramagnetic, dark-green bis-cyclopentadiene titanium. The behavior of the resulting phenyl radicals depends on the type of solvent: in benzene, they yield diphenyl, whereas in alcohol solutions or in chloroform they attract the hydrogen to form benzene. All reactions mentioned remind one very much of the thermo- and photoreactions of diphenyl mercury with alcohols, with CCl_4, and with chloroform, which proceed according to a free-radical mechanism. There are 5 references: 1 Soviet and 1 US.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii Gor'kovskogo gosudarstvennogo universiteta im. N.I. Lobachevskogo (Scientific Research Institute of Chemistry of the Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: June 16, 1960

RAZUVAYEV, G.A.; PETUKHOV, G.G.; ZHIL'TSOV, S.F.; KUDRYAVTSEV, L.F.

Oxidation of dicyclohexylmercury. Dokl. AN SSSR 135 no.1:87-90 N'60. (MIRA 13:11)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N.I.Lobachevskogo. 2. Chlen-korrespondent AN SSSR (for Razuvayev).
(Mercury)

RAZUVAYEV, G.A.; PETUKHOV, G.G.; KAPLIN, Yu.A.

Reactions of diphenylmercury with benzene. Dokl. AN SSSR 135 no.2:342-345 N '60. (MIRA 13:11)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im.N.I.Lobachevskogo. 2. Chlen-korrespondent AN SSSR (for Razuvayev).
(Mercury) (Benzene)

S/081/62/000/022/027/088
B144/B101

AUTHORS: Vyazankin, N. S., Razuvayev, G. A., Dergunov, Yu. I.

TITLE: Effect of metallic lead and hexaethyldiplumbane on the decomposition of stabilized tetraethyl lead

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 22, 1962, 228, abstract 22Zh244 (Tr. po khimii i khim. tekhnol. [Gor'kiy], no. 3, 1961, 652-655)

TEXT: A mixture of tetraethyl lead (III) and highly dispersed Pb was obtained from $(C_2H_5)_3PbPb(C_2H_5)_3$ (I) under the effect of 2-3% by weight of C_2H_4Br (II) ($\sim 20^{\circ}C$, 24 hrs). Decanted III, with an admixture of II (5-10% by weight of the initial amount) in another case a nonseparated mixture of II, III and Pb, was kept 4 hrs at 135°C, all contact between the reaction mixture and the air moisture being prevented. It has been found that II prevents the thermal decomposition of III, but that Pb weakens this effect considerably. For this reason additions of I to a mixture of III and II (% by weight of I and II: 3.1-8.6; 1.8-2.1,

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B144/B101

Effect of metallic lead and ...

respectively) caused III to decompose (135°C). The decomposition of III under the action of Pb is not accompanied by an accumulation of I as intermediate. [Abstracter's note: Complete translation.]

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S/030/61/000/004/013/015
B105/B206

AUTHORS: Razuvayev, G. A., Corresponding Member AS USSR, Latyayeva, V. N., Candidate of Chemical Sciences, Brilkina, T. G., Candidate of Chemical Sciences

TITLE: Homolytic reactions in the liquid phase

PERIODICAL: Vestnik Akademii nauk SSSR, no. 4, 1961, 124-127

TEXT: The first simpozium po gomoliticheskim reaktsiam v zhidkoy faze (Symposium on Homolytic Reactions in the Liquid Phase) held in Gor'kiy and Dzerzhinsk from December 7-10, 1960, is described. The Symposium which was attended by about 500 chemists, was convened by the Nauchnyy sovet po teorii khimicheskogo stroyeniya, kinetike i reaktsionnoy sposobnosti Otdeleniya khimicheskikh nauk Akademii nauk SSSR (Scientific Council for the Theory of Chemical Structure, Kinetics and Reactivity of the Department of Chemical Sciences AS USSR), the Gor'kovskiy nauchno-issledovatel'skiy institut khimii (Gor'kiy Scientific Research Institute of Chemistry) and the oblastnoye otdeleniye Vsesoyuznogo khimicheskogo obshchestva im. D. I. Mendeleyeva (Rayon Department of the All-Union Chemical Society imeni D. I. Men-

Homolytic reactions ...

deleyev). The following reports are mentioned: By the method of electronic paramagnetic resonance, V. V. Voyevodskiy clarified the structure of benzene chromate cations as well as the aromatic ionic radicals, and established the formation of hydrogen atoms during the irradiation of the system Fe^{2+} $+H_2SO_4+H_2O$ at 77°K by means of ultraviolet light; M. B. Neyman, A. L. Buchachenko reported on the formation of stable radicals which can serve as basis for the determination of active, short-lived radicals; A.N. Terenin, B. L. Kurbatov, R.F. Vasil'yev, A.A. Vichutinskiy, O.N. Karpukhin, L.M. Postnikov, and V.Ya. Shlyapintokh reported on the method of chemiluminescence; K.S. Bagdasar'yan, R.I. Milyutinskaya, E.A. Trosman, and V.A. Borovkova investigated the reactions of the phenyl- and nitrophenyl radicals with aromatic compounds by the kinetic method; V. F. Tsepalov found an expression for the rate of consumption of an arbitrary component as function of the concentration of reacting substances; N.M. Emanuel' discovered the dependence of the oxidizing of liquefied hydrocarbon on the concentration of the solvent; N. M. Emanuel', E. K. Mayzus, and I. P. Skibida reported on the production of alcohols and ketones according to the chain- and molecular method of the oxidation of n-decane; B. V. Yerofeyev reported on complementing the previous theory of primary initiating by a secondary initiating; K. I. Ivanov and Ye. D.

Homolytic reactions ...

Vilyanskaya showed that aniline added to an oil already in a state of oxidation is converted into a product behaving similar to a peroxide radical which accelerates the reaction; B. A. Redoshkin and V. A. Shushunov showed the dual effect of metal salts of variable valency; A [illegible] Buchachenko, M. P. Neyman, and K. Ya. Kaganskaya determined the average lifetime of peroxide radicals of trimethyl heptane (3.5 sec); I. V. Berezin, K. Vatsek, Go Chu, and N. F. Kazanskaya classified a number of free radicals according to their kinetic indices; Ye. N. Gur'yanova, I. G. Chernomorskaya, and M. S. Fel'dshteyn discovered the direct dependence between exchangeability of the compounds S-S, S-N, S-C and their vulcanizing activity; G. A. Razuvayev, G. G. Petukhov, Ye. V. Mitrofanova, and V. N. Latyayeva showed that the use of isotope methods permits the discovery of new reactions during the oxidation of organometallic compounds, which cannot be determined by other methods; V. A. Shushunov, Yu. A. Aleksandrov, and T. G. Brilkina submitted a scheme of the oxidation process of the organometallic compounds investigated; N. S. Vyazankin, G. A. Razuvayev, Yu. I. Dergunov, and O. A. Shchepetkova reported on the homolytic cleavage of elementary compounds; Yu. A. Ol'dekop and N. M. Mayer reported on the mechanism of the homolytic synthesis of organometallic compounds; N. P. Khyrak and V. A. Pal'm reported on the homo-

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Homolytic reactions ...

lytic character of the formation of organomagnesium compounds: A. V. Savitskiy and Ya. K. Syrkin reported on the spectrophotometric investigations which were utilized for determining the thermodynamic indices of the oxidation reactions of ferrocene and rutheniumcene by means of iodine; G. I. Nikishin and V. D. Vorob'yev reported on the linkage of the alcohols C_5-C_{10} to α-olefins of the composition C_6-C_{13}; G. I. Nikishin, Yu. N. Ogibin, and A. D. Petrov reported on esters of dicarboxylic acids which are linked to γ-olefins under formation of esters of α-alkyl carboxylic acids; G. A. Razuvayev and L. S. Boguslavskaya reported on the production of glycol esters; M. G. Gonikberg and V. M. Zhulin reported on the production of an unstable polymer at a pressure of 5000 kg/cm^2, which is depolymerized at customary pressure; A. P. Meshcheryakov and I. Ye. Dolgiy reported on the production of substituted cyclopropane derivatives by addition of methylene radical and its derivatives on alkene; A. N. Nesmeyanov, R. Kh. Freydlina, V. N. Kost. M. Ya. Khorlina, T. T. Sidorova, R. G. Petrova, and A. B. Terent'yev arranged the investigated radicals according to their relative stability; M. F. Shostakovskiy, Ye. N. Prilezhayeva, and L. V. Tsymbal reported on heterolytic reactions of the additions which are strictly subordinated to the rule of transaddition; G. M. Strongin reported on the conforma-

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S/030/61/000/004/013/015
B105/B206

Homolytic reactions ...

tion of products of the homolytic addition of chlorine on benzene. The delegates of the Symposium expressed the wish to discuss regularly chemical problems connected with the homolytic reaction in the liquid phase.

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RAZUVAYEV, G.A.; ETLIS, V.S.; GROBOV, L.N.

Preparation of cyclic alkenethiocarbonates. Zhur.VKHO 6 no.5:588-589 '61. (MIRA 14:10)

(Carbonic acid)

26294
S/190/61/003/008/007/019
B110/B218

15,8050

AUTHORS: Razuvayev, G. A., Etlis, V. S., Kirillov, N. I., Samarina, Ye. M.

TITLE: New peroxide compounds obtained on the basis of cyclic ketones as initiators for polymerization of vinyl compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 8, 1961, 1176-1180

TEXT: Since arylated or acylated derivatives of hydroxycyclohexyl hydroperoxides are good initiators for radical polymerizations, the authors aimed at synthesizing alkyloxy formylated derivatives of bis-(1-hydroperoxycycloalkyl)-peroxides having the general formula $R_1O-\overset{O}{\overset{\|}{C}}-OO-R_2-OO-R_2-OO-\overset{O}{\overset{\|}{C}}-OR_1$, where $R_1 = CH_3$, C_2H_5, C_6H_{11}; R_2 = gem-cyclohexyl and gem-cyclopentyl. Synthesis proceeded according to the equation: $MeOO-R_2-OO-R_2-OOMe + 2\ R_1O-\overset{O}{\overset{\|}{C}}-Cl \rightarrow R_1O-\overset{O}{\overset{\|}{C}}-OO-R_2-OO-R_2-OO-\overset{O}{\overset{\|}{C}}-OR_1 + 2\ MeCl$; (Me = alkali metal). It was performed under virulent stirring in

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New peroxide compounds obtained on ...

low-boiling hydrocarbons which served as a medium, and at a temperature of T $\sim 5^{\circ}$C. The alkali salts of the initial dihydroperoxides were obtained in ether solution from the hydroxides of the alkali metals and bis-(1-hydroperoxycycloalkyl)-peroxide. The following structural formulas of the peroxides synthesized are given:

X

New peroxide compounds obtained on ...

The authors also made an attempt to obtain bis-1(-alkylpercarbonate-cycloalkyl)-peroxides directly from the hydroperoxides and esters of chlorocarbonic acid, in the presence of pyridine, which failed since the final product could not be isolated in pure form. The compounds synthesized are white, crystalline substances, readily soluble in diethyl ether, acetone, benzene, poorly soluble in alcohols and hydrocarbons, and unsoluble in H_2O.

The substance decomposes at melting temperature and explodes above 150°C, especially on friction or impact. Measurements of the polymerization rate of vinyl chloride (10% at 45°C, 0.05 mole% of initiator) and of methyl methacrylate led to the following results: (1) the initial bis-(1-hydroperoxycycloalkyl)-peroxides exhibit the same initiating effect as benzoyl peroxide; (2) bis-(1-alkylpercarbonate-cyclohexyl)-peroxides have the two-fold, and (3) the corresponding cyclopentyl compounds have the three-fold initiating effect as compared to benzoyl peroxide. In addition, the authors found that with both cyclohexyl and cyclopentyl compounds the above effect depended on R_1 in the following order: $C_6H_{11} < C_2H_5 < CH_3$. There are 1 figure, 2 tables, and 8 references: 2 Soviet and 6 non-Soviet.

Card 4/5

New peroxide compounds obtained on ...

The three most important references to English-language publications read as follows: Ref. 1: W. Cooper, J. Chem. Soc., 1951, 1340; Ref. 5: M. S. Kharasch, G. Sosnovsky, J. Org. Chem., 23, 1322, 1958; Ref. 8: N. Milas, J. Amer. Chem. Soc., 61, 2430, 1939.

SUBMITTED: October 7, 1960

Card 5/5

RAZUVAYEV, G.A.; PETUKHOV, G.G.; DODONOV, V.A.

Mechanism of the chain termination reaction in the radical polymerization of vinyl chloride in the presence of C^{14} tagged initiators. Vysokom.soed. 3 no.10:1549-1553 O '61. (MIRA 14:9)

1. Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete imeni N.I. Lobachevskogo.
(Vinyl compound polymers) (Carbon--Isotopes)

3090
S/190/61/003/012/004/012
B101/B110

15.8610 2209

AUTHORS: Lapshin, N. M., Moryganov, B. N., Razuvayev, G. A., Ryabov, A. V., Khidekel', M. L.

TITLE: Nitrogenous peroxide compounds as initiators of polymerization of vinyl monomers. I

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 12, 1961, 1794 - 1799

TEXT: On the basis of literature data stating that the initiating activity of peroxide compounds is intensified by addition of amines, the authors investigated the initiating effect of peroxides which already contain amine or amide groups in their molecules. Initiators were synthesized as follows: Cumyl-N-phenyl peroxy carbamate and hexamethylene-N,N'-bis-α-cumyl-peroxy carbamate according to Refs. 6, 7 (see below), the other peroxide compounds according to A. Rieche et al. (Chem. Ber., 92, 1206, 1959). N,N'-bis-(cumyl peroxy methyl)-urea was first synthesized by the authors: urea was shaken in 2 N H_2SO_4 with cumyl peroxide and formalin. After 12 hr storing in the refrigerator, the peroxide crystallized out

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30910
S/190/61/003/012/004/012
B101/B110

Nitrogenous peroxide...

(melting point 120 - 121°C, yield 42%). The initial rate of polymerization of monomers cleaned in vacuum by distillation: methyl methacrylate (MMA); methacrylic acid (MA); acrylonitrile (AN); styrene (St) was measured dilatometrically. Results are given in a table. Polymerization was achieved in bulk. A distinct dependence of the initiating effect on the structures of peroxides was found. Peroxides with group $>N-CO-O-O$ were more active than peroxides with group $>N-CH_2-O-O$. Furthermore, the nature of the monomer especially the chemical nature of the groups between the nitrogen atom and the peroxide group influences the initiating effect of peroxides. The optimum temperature for polymerization also depended on structure of monomer and peroxide. Peroxides with group $>N-CH_2-O-O$ were most effective at elevated temperatures (St: $\geq$120°C) while the optimum temperature for cumyl N phenyl peroxy carbamate (for MMA, MA, and AN) was 20 - 60°C. The insignificant activity of this compound in polymerization of styrene (120°C) is ascribed to its low temperature stability. The initial rate of polymerization depended on temperature according to the Arrhenius equation. The activation energy was 17.4 kcal/mole. For the dependence of the initial rate v_{in} on the concentration c_I of the initiator

Card 2/

Nitrogenous peroxide...

(in the concentration range $0.187 \cdot 10^{-3}$ to $0.44 \cdot 10^{-3}$ molar parts), it was found: $v_{in} = 3.5\sqrt{c_o} + 0.0448$. There are 5 figures, 1 table, and 9 references: 2 Soviet and 7 non-Soviet. The three references to English-language publications read as follows: Ref. 3: M. Imoto, S. Choe, J. Polymer Sci., 15, 485, 1955; Ref. 6: E. L. O'Brien, T. M. Beringer, R. B. Mesrobian, J. Amer. Chem. Soc., 79, 6238, 1957; Ref. 7: C. Y. Pedersen, J. Organ. Chem., 23, 252, 1958.

ASSOCIATION: Nauchno-issledovatel'skiy institut khimii pri Gor'kovskom gosudarstvennom universitete im. N. I. Lobachevskogo (Scientific Research Institute of Chemistry at the Gor'kiy State University imeni N. I. Lobachevskiy)

SUBMITTED: January 5, 1961

Table. Initial rates of polymerization of MMA, MA, AN, and St with initiation by means of nitrogenous peroxides.

Legend: (A) Initiator; (B) formula; (C) concentration c_o of the initiator,

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Nitrogenous peroxide...

moles/1000 g of monomer; (D) initial rate v_H (= v_{in}) of polymerization, % of conversion/min·10; (a) MMA at 60°C; (b) MA at 60°C; (c) AN at 50°C; (d) St at 120°C; (e) does not initiate; (1) cumyl-N-phenyl peroxy carbamate; (2) N-cumyl peroxy methyl benzamide; (3) bis-benzaminomethyl peroxide; (4) hexamethylene-N,N'-bis-α-cumyl peroxy carbamate; (5) N,N'-bis-(cumyl-peroxy-methyl)-urea; (6) bis-(dicyclohexyl aminomethyl)-peroxide; (7) cumyl peroxy methyl dimethylamine; (8) cumyl peroxy methyl dicyclohexylamine.

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RAZUVAYEV, G.A.; TERMAN, L.M.

Decomposition of dicyclohexylperoxydicarbonate in solution in the presence of certain metals and metal salts. Zhur.VKHO 6 no.4:473-474 '61. (MIRA 14:7)

1. Gor'kovskiy gosudarstvennyy universitet.
(Peroxydicarbonic acid) (Organometallic compounds)

RAZUVAYEV, G.A.; OSANOVA, N.A.; SHULAYEV, N.P.; TSIGIN, B.M.

Radical reactionsof pentaphenylantimony. Zhur.ob.khim. 30 no.10: 3234-3237 O '61. (MIRA 14:4)

1. Gor'kovskiy gosudarstvennyy universitet.
(Antimony organic compounds)

S/079/61/031/001/023/025
B001/B066

AUTHORS: Razuvayev, G. A., Latyayeva, V. N., and Petukhov, G. G.

TITLE: Decomposition of Acyl Peroxides in Acid Medium

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 268 - 274

TEXT: Refs. 1 and 2 indicate the possibility of a regenerative exchange in carboxylic acids $RCOO^{\cdot} + R'COOH \longrightarrow RCOOH + R'COO^{\cdot}$ (1), but so far this could not be confirmed experimentally. On the basis of Refs. 1 - 5, the authors tried once more to establish the so-called "relay-transfer" of the acyloxy radicals (1) in carboxylic acids. For this purpose, the reaction of benzoyloxy- and m-nitro-benzoyloxy radicals which are more stable than the acetyloxy radicals was carried out in acetic and benzoic acid C^{14}-labeled in the carboxyl. The separation of labeled $C^{14}O_2$ may indicate the occurrence of such an exchange, provided that the initial acids and the resultant products are stable to CO_2 separation during the course of reaction. A spontaneous decarboxylation of acetic and benzoic acid at 100°C is im-